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Kinetics of the chlorination of hematite

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Abstract

The chlorination of hematite was studied by thermogravimetry between 600 and 950°C. The role of convective mass transfer into the boundary layer surrounding the sample, gaseous diffusion into the sample pores, and the effect of the reaction temperature on the reaction rate were analyzed in order to determine the rate-controlling regime. In the 750–950°C temperature range, the reaction rate was significantly affected by diffusion of Cl_2 through the gas film surrounding the sample. In the 600–750°C range a mixed rate-controlling regime with an apparent activation energy of 200 kJ mol^{-1} was observed. The diffusion of iron chlorides and oxygen out of the sample pores is proposed as the slowest diffusion step.

Keywords: Chlorination; Hematite; Intrinsic kinetics; Reaction rate; Thermogravimetry

List of symbols

A	solid sample area/(m^2)
D	diffusion coefficient/(m^2 s^{-1})
E_α	activation energy/(kJ mol^{-1})
ΔG°	standard Gibbs energy/(kJ mol^{-1})
L	characteristic dimension of the sample/(m)
M_i	initial mass/(mg)
ΔM	mass loss/(mg)
N	molar flow of chlorine/(mol s^{-1})
NTP	normal temperature and pressure

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p	pressure/(kPa)
ΔP	gradient of partial pressure/(kPa)
R	gas constant/(m^3 kPa K^{-1} mol^{-1})
Re	Reynolds number/(dimensionless)
r	reaction rate/(mol s^{-1})
Sc	Schmidt number/(dimensionless)
T	absolute temperature/(K)
t	time of reaction/(s)
U	flow rate/(m^3 s^{-1})
α	conversion/(dimensionless)
ν	kinematic viscosity/(m^2 s^{-1})

1. Introduction

The chlorination of hematite, Fe_2O_3, has not been studied extensively [1–4]. Bertóti et al. have determined that the chlorination of Fe_2O_3 powder started at 527°C [1]. The apparent activation energy was 188 kJ mol^{-1} in the 600–780°C temperature range, but the authors have indicated that the reaction rate might be influenced by mass transport [1]. Fruehan and Martonik [2] have studied the rate of chlorination of pellets of Fe_2O_3 between 800 and 1200°C. The authors have observed that below 1000°C pore diffusion was the rate-limiting whereas at higher temperatures the rate was controlled by diffusion of Cl_2 through the gas-film boundary layer around the pellet [2]. Szekely et al. [3] have also reported that the Fe_2O_3–Cl_2 reaction was controlled by mass transfer at high temperatures and moderate pellet sizes. Recently, it was determined that the reaction of Cl_2 with hematite powder takes place above 600°C and that the reaction products are totally gaseous [5].

Most studies focusing on the kinetics of the Cl_2–Fe_2O_3 reaction have reported the strong influence of mass transfer on the reaction rate [1–4]. Such results were observed for the chlorination of both single solid pellets [2, 3] and powders [1, 4]. However, the role of mass transport on the reaction-rate-controlling regime and the identity of gaseous species controlling diffusion is not clearly understood. This is in part due to the very little available kinetic information but largely it is a consequence of the fact that some authors did not provide details of the experimental conditions used in their studies. Due to the number and complexity of factors influencing solid–gas reactions, such as temperature, flow rate of reacting gas, surface characteristics, impurity content, size and shape of the particles, pore volume and distribution, etc, the identification of the rate-controlling regime is strongly dependent upon the type of sample and experimental conditions.

The purpose of this paper is to improve the understanding of the chlorination kinetics of Fe_2O_3 by studying the effect of experimental conditions on the rate-controlling regime. Therefore, the convective mass transfer through the diffusion layer formed around the sample, the role of gaseous diffusion into the pores of Fe_2O_3 powder, and the effect of temperature on the reaction rate were studied. The chlorination of Fe_2O_3 powder was followed by thermogravimetry between 600° and 950°C by varying the flow rate of Cl_2, the sample size, the type of crucible, and the reaction temperature; the effect of addition of chemically inert powders was also investigated.

2. Rate-controlling regimes in solid–gas reactions

Kinetic studies carried out by thermogravimetric techniques, as will be presented in this paper, should take into account that typical experiments involve a gas flowing to the sample contained within a crucible [6,7]. The gases in contact with the reacting solid are slowed down by the effects of friction and thus the reacting gas must be transported across the resulting boundary layer around the sample. Gaseous mass transfer from the bulk gas to the sample can control the reaction rate in two ways: gas starvation and convective mass transfer. Gas starvation takes place in experiments performed with low flow rates when the reaction rate is equal to or more rapid than the velocity of the gas supply. Thus, the overall reaction rate depends linearly on gas flow rate. When starvation effects are absent, mass transfer through the boundary layer around the reacting solid can be rate-controlling. In this case the overall reaction rate for reactions of equimolar counter diffusion depends on the gas flow rate through the following equation [3,8]:

$$N = D(2.0 + 0.6\,Re^{1/2}Sc^{1/3})\Delta PA/LRT \qquad (1)$$

where N refers to the molar flow of reacting gas and $Re, = U \cdot L/\nu$, and $Sc, = \nu/D$, represent the Reynolds and Schmidt numbers, respectively. Although more rigorous expressions have been reported [3,9], Eq. (1) gives a good approximation for the analysis of thermogravimetric experiments presented in this paper.

Mass transfer into the pores of the sample can also be the rate-controlling step. This occurs when the mass transfer into the pores of the sample is the slowest step. A standard technique for studying the role of mass transfer in powders is through the analysis of the effect of the thickness of the reaction bed on the reaction rate. In thermogravimetry this is performed by varying the sample mass in a given crucible. When reaction rate decreases with increasing the powder mass, pore diffusion is rate-controlling provided that the interface area of reaction is proportional to the sample mass, as can be expected for fine powders.

Thermogravimetry also provides two alternative procedures for changing gas diffusion into reacting powders. One way is through the type of crucible [6,7,10] and another is by means of mixing the reacting powder with a chemically inert powder [6,7]. Both procedures alter the gas transport into the sample pores and the reaction rate is changed provided that gas diffusion is the rate-limiting step.

The reaction temperature may determine a change in the rate-controlling regime of any solid-gas reaction. At high temperature chemical reactions are rapid and thus diffusion control is highly probable. At low temperature chemical control is very probable. When the chemical reaction is rate-controlling, the rate of change of chemical reaction rate with temperature is exponential, following an Arrhenius expression. The reaction rate, r, may be expressed to a first approximation as:

$$r = d\alpha/dt = K(T)F(P)G(\alpha) \qquad (2)$$

where $K(T)$ represents the Arrhenius function, and $F(P)$ and $G(\alpha)$ are functions depending on gas composition and conversion, α. For the chlorination of Fe_2O_3, the true activation energy and $F(P)$ and $G(\alpha)$ functions are completely unknown.

3. Experimental

The gases used were argon, 99.99% purity (AGA, Argentina), and Cl_2, 99.8% purity (Indupa, Argentina). The starting materials were Fe_2O_3 (Spex Industries, Inc., USA), TiO_2 (Mallinckrodt Chemical Works, USA) and Al_2O_3 (Berna, Argentina). Thermogravimetric samples were pure Fe_2O_3 (BET surface area of 3.0 $m^2\,g^{-1}$) and Fe_2O_3–TiO_2 and Fe_2O_3–Al_2O_3 mixtures in the ratio 3/7 and 1/4, respectively.

The mass changes occurring during the chlorination of the samples indicated above were measured using a thermogravimetric analyzer (TGA), which has been extensively elsewhere [11]. This thermogravimetric analyzer consists of an electrobalance (Model 2000, Cahn Instruments, Inc.) suitable for working with corrosive atmospheres, a gas line, and a data acquisition system. This experimental set-up has a sensitivity of $\pm 5\,\mu g$ while operating at 950°C under a flow rate of 8 L h^{-1} (NTP), which is the maximum flow rate possible in the experimental design used in this study.

The thermogravimetric procedure was as follows. Samples — between 1.2 and 40 mg — were placed in a quartz crucible under flowing Ar and kept for 2 h at the reaction temperature. Chlorine was then introduced and mass changes were measured. Isothermal experiments were performed at several flow rates by keeping the chlorine partial pressure constant. For convenience, mass changes were plotted as fractional mass loss $\Delta M/M\mathrm{i}, = -\alpha$, as a function of time. Such plots, i.e. $\Delta M/M\mathrm{i}$ vs t, corrected by apparent mass changes [11], were used for discussing the effect of the kinetic variables on r. Two types of crucible were also used. One was a hemispherical crucible with a diameter of 0.9 cm, and the other a flat crucible with a side of 1.1 cm and 0.2 cm height. The characteristic dimension L of the sample is calculated as the diameter of sphere that has the same area as that of the free surface of our samples. For 2 mg of sample, the values obtained are $L = 0.25$ cm and $L = 0.62$ cm for the samples in the hemispherical and flat crucibles, respectively.

4. Results and discussion

The chlorination of Fe_2O_3 can produce three gaseous species above 600°C: $FeCl_2$, $FeCl_3$ and Fe_2Cl_6 [1, 12]. No evidence of intermediate solid compounds has been reported in previous studies [1, 2, 4, 5]. Therefore, the reaction continuously progresses with mass loss. The equilibrium pressures of $FeCl_3(g)$ and $Fe_2Cl_6(g)$ are given by: $\log[p^2(FeCl_3)/p(Fe_2Cl_6)] = 6907/T + 10.267$, where the values of $p(FeCl_3)$ and $p(Fe_2Cl_6)$ are expressed in kPa [13]. Therefore the chlorination of Fe_2O_3 is represented by:

$$Fe_2O_3(s) + 3Cl_2(g) \rightleftharpoons 2FeCl_3(g) + 3/2O_2(g) \qquad \text{(I)}$$

$$2FeCl_3(g) \rightleftharpoons Fe_2Cl_6(g) \qquad \text{(II)}$$

Although the standard Gibbs energy ΔG° of reaction I [14], viz. $\Delta G^\circ = -0.384\,T + 571/934$ kJ mol^{-1} of Cl_2, is positive at the temperatures studied in this paper, the reaction takes place in flowing Cl_2 above 600°C due to the continuous removal of O_2 and Fe_2Cl_6 [5].

As reported in various studies, mass transfer into the gas boundary layer surrounding Fe_2O_3 samples has played an important role in controlling the chlorination rate [1–3]. For this reason the effect of flow rate at 850 and 750°C was first analyzed in this study. A small sample, about 2.2 mg, was used in order to minimize concentration gradients of gaseous species and temperature. Fig. 1 illustrates experiments at various flow rates of Cl_2 by keeping the partial pressure (pCl_2) constant at two temperatures. At 850°C, experiments were performed at three flowrates: 1.14, 3.56, and 4.33 L h^{-1} with $pCl_2 = 65$ kPa, as shown in Fig. 1A. As the flow rate was increased, the rate of mass loss was more rapid. For instance, a conversion of 0.6 was achieved in about 190 s and 150 s for flow rates of 1.14 and 4.33 L h^{-1} respectively. So r increases with increase of the Cl_2 flow rate. Thus, the rate-controlling regime depends on mass transfer in the gaseous phase at 850°C.

Fig. 1B shows the effect of flow rate on the fractional mass loss at a lower temperature and a lower chlorine partial pressure, i.e. 750°C and $pCl_2 = 35$ kPa. A conversion of 0.6 was achieved in approximately 1200s for 2.08 L h^{-1}, which indicates a significant decrease in the chlorination rate with temperature as compared

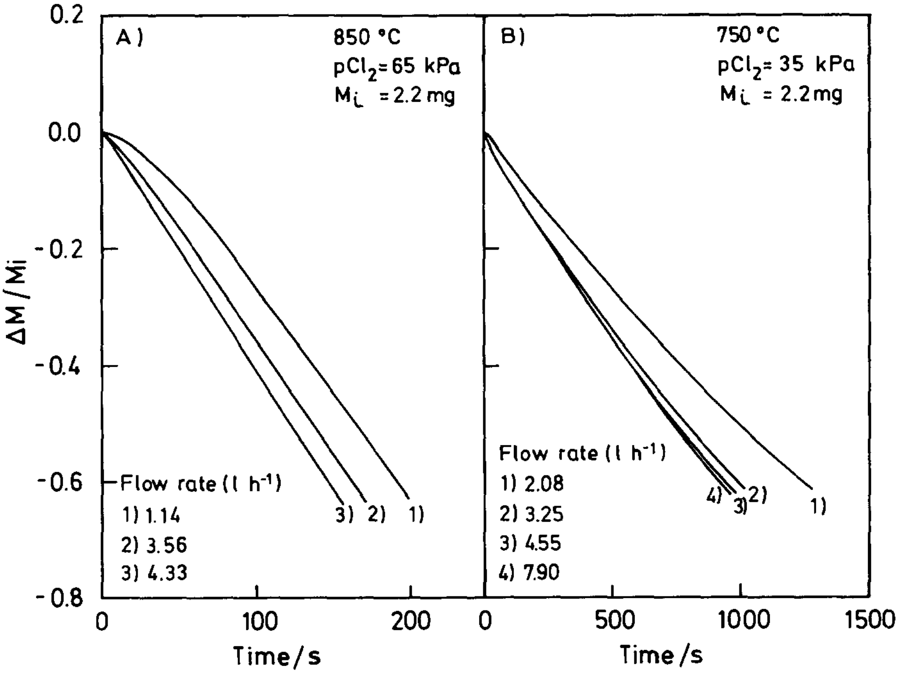

Fig. 1. Effect of flow rate of chlorine on the chlorination of Fe_2O_3 at two temperatures. Samples were contained within a hemispherical crucible (diameter 0.9 cm).

with Fig. 1A. Thus, the intrinsic reactivity of the solid is strongly affected by the temperature. When the flow rate was increased from 2.08 to 3.25 L h^{-1} the reaction time decreased for the same conversion and thus the reaction rate was noticeably more rapid (curve 2 of Fig. 1B). However, when the flow rate was increased from 3.25 to 4.55 L h^{-1} only little effect was observed on the chlorination rate and finally between 4.55 L h^{-1} and 7.90 L h^{-1} no difference between the corresponding curves was observed. Therefore, within the experimental uncertainty, the reaction rate was nearly constant at flow rates between 4.55 L h^{-1} and 7.9 L h^{-1}.

As discussed by Hills [8], when variations in the flow rate of the reacting gas do not produce significant changes in the reaction rate, it may be concluded that reacting gas starvation is absent. Hence, the experiments shown in Fig. 1B enable one to conclude that the rate of chlorine supply above 4.55 L h^{-1} is high enough for avoiding starvation effects in Fe_2O_3 chlorination at 750°C. On the other hand, convective mass transfer through the boundary layer surrounding the sample may play a relevant role in reaction rate control even at a flow rate of 7.9 L h^{-1}. In order to analyze this possibility the molar flux of chlorine, N, through the boundary layer was evaluated by using Eq. (1). Values of D and v are given in Table 1 for $pCl_2 = 35$ kPa and various temperatures, as calculated from the theory of Chapman–Enskog [3,9]. Thus, values of N for two flow rates and two types of crucible were estimated. Table 1 shows that the flow rate and the temperature have negligible effect on the molar flux. The molar flux for the hemispheric crucible is approximately of the order of 2×10^{-6} moles of Cl_2 per second under various experimental conditions.

A mean value of the reaction rate at $\alpha = 0.6$, can be estimated from Fig. 1B. At 750°C and 7.9 L h^{-1} this results in $r = 2.75 \times 10^{-8}$ moles of Cl_2 per second. This value is about two orders of magnitude greater than the value calculated by using Eq. (1) (see Table 1), which might indicate that convective mass transfer is not rate-controlling. However, this comparison is not rigorously correct since values obtained by using Eq. (1) are only approximate. Eq. (1) is valid for a pellet in a freely flowing gas and not for a sample contained within a crucible. Some authors have indicated that, in practice, mass transfer rates into powders contained within crucibles are more than one order of magnitude lower than the values given by Eq. (1) [8, 15]. Moreover, Hakvoort has determined that the mass transfer can be 80 times lower than for a free hanging sphere [15]. Following Refs. [8] and [15], the convective mass transfer should be

Table 1
Calculated molar flow of chlorine, N (mol s^{-1}), as a function of temperature, flow rate, and type of crucible for $P(Cl_2) = 35$ kPa. The flow rates (4.55 and 7.9 L h^{-1}) were measured at NTP.

T^a/°C	$10^4 \times D^a$/ ($m^2 s^{-1}$)	$10^4 \times v^a$/ ($m^2 s^{-1}$)	Hemispherical crucible		Flat crucible	
			N^a(4.55 L h^{-1})	N^a(7.9 L h^{-1})	N^a(4.55 L h^{-1})	N^a(7.9 L h^{-1})
600	0.763	0.645	1.7×10^{-6}	1.8×10^{-6}	4.6×10^{-6}	4.9×10^{-6}
750	0.995	0.830	1.9×10^{-6}	2.0×10^{-6}	5.1×10^{-6}	5.4×10^{-6}
950	1.35	1.12	2.1×10^{-6}	2.2×10^{-6}	5.7×10^{-6}	6.0×10^{-6}

[a] See "List of symbols" for definitions.

between 2.0×10^{-7} and 2.5×10^{-8} mol s^{-1}, which is very near to the value of r. Accordingly, we assumed that convective mass transfer is certainly minimized in the experimental design of the study for a flow rate of 4.55 L h^{-1} at 750°C, but it might be significant in controlling the reaction rate. However, it will be shown later that the effect of Cl_2 flow rate is negligible at temperatures lower than 750°C.

4.1. Analysis of mass transfer through the sample pores

Considering that powders adopt the shape of the crucible, so that the thickness of sample is affected, two types of crucible were used in order to study the effect of the diffusion into the sample pores on the reaction rate. Fig. 2 shows thermogravimetric curves for chlorinations of various sample masses for two types of crucible. Fig. 2A shows that samples of 4.78, 3.19 and 1.23 mg contained within a hemispherical crucible achieved a conversion of 0.6 in 1520, 1200 and 1050 s, respectively. Hence, as the sample mass decreases the reaction rate increases. Therefore, the amount of powder contained in such a crucible, which forms a hemispherical packing at the bottom, affects the reaction rate so mass transport into the sample pores is rate-controlling.

Fig. 2B shows thermogravimetric curves obtained by chlorination of various sample masses contained within a flat crucible but otherwise keeping the same experimental

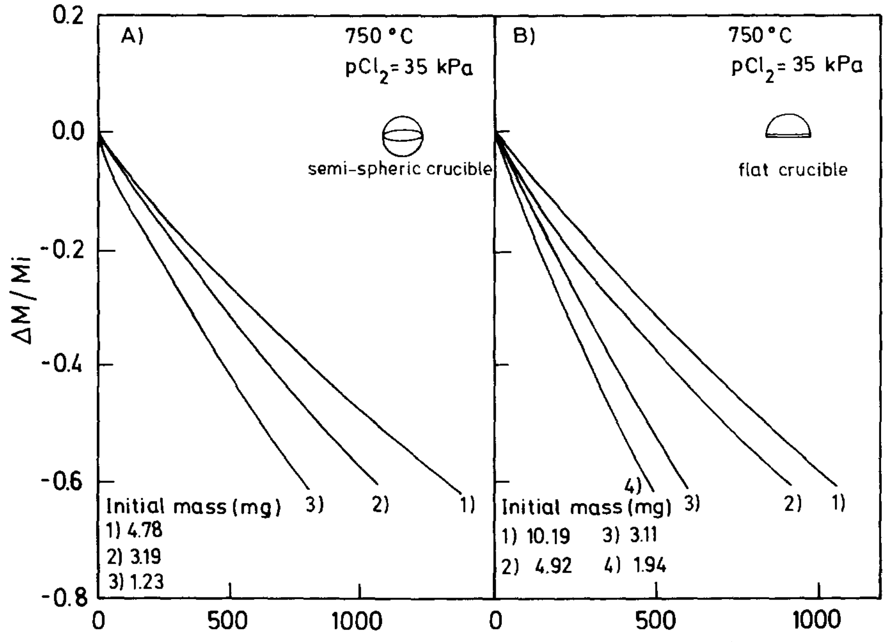

Fig. 2. Effect of sample mass on the chlorination of Fe_2O_3 contained in two different crucibles: (A) hemispherical crucible (diameter) 0.9 cm); (B) flat crucible (bottom: 1.1×1.1 cm^2; height 0.02 cm).

conditions as for Fig. 2A. The use of the flat crucible has the advantage of better accessibility of Cl_2 since the powder covers a greater area forming a very thin (less than 0.05 cm) layer. However a significant dependence of the reaction rate on the amount of sample was observed. When samples were changed from 10.2 to 1.94 mg the reaction rate was progressively more rapid. For 10.2 mg, $r = 1.03 \times 10^{-7}$ mol s^{-1} and for 1.94 mg, $r = 4.5 \times 10^{-8}$ mol s^{-1}. A comparison of r with the respective values of molar flux for the flat crucible given in Table 1 also indicates that for this crucible convective mass transfer might be important to rate-control. Accordingly, two types of mass transfer may affect the chlorination rate of Fe_2O_3 at 750°C: mass transfer through the boundary layer and into the sample pores.

4.2. *Analysis of the effect of temperature on the reaction rate*

Fig. 3 illustrates the effect of the temperature on the chlorination of 2 mg of Fe_2O_3 contained within the flat crucible by keeping a flow rate of 4.55 L h^{-1} and a $pCl_2 = 35$ kPa. The reaction is more rapid as the temperature increases. However, above 700–750°C the effect of the temperature is less important. This behavior is consistent with the increasing importance of mass transfer in the gaseous phase on the reaction rate as the temperature increases, as discussed in relation to Figs. 1 and 2.

The significant effect of the temperature on the reaction rate below 750°C suggests a high activation energy (E_a). The calculation of such a kinetic parameter can be

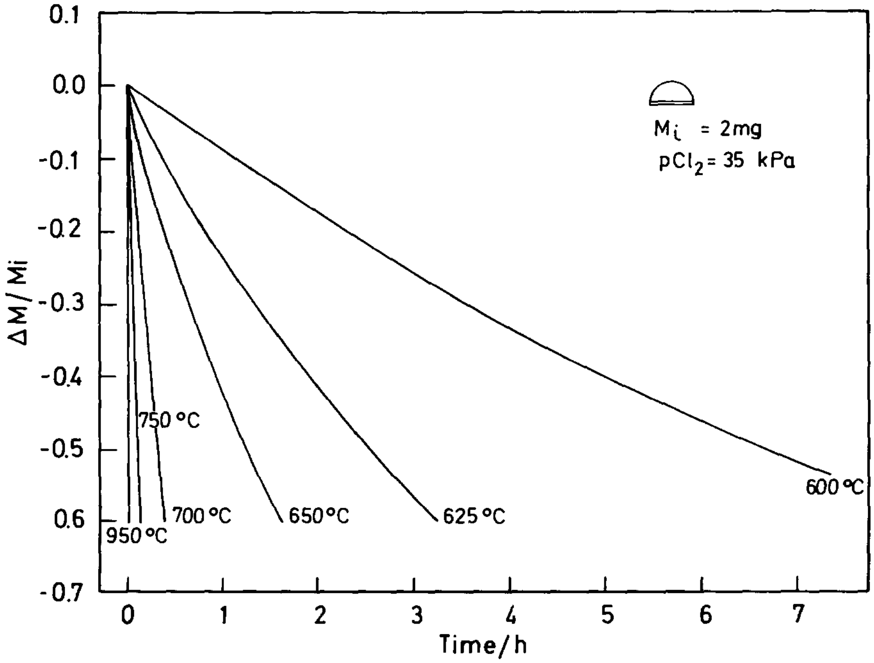

Fig. 3. Effect of the temperature on the chlorination of 2 mg of Fe_2O_3 contained within the flat crucible.

achieved by use of Eq. (2). Although the $G(\alpha)$ function is unknown, a common approach for evaluation of the activation energy is to substitute the $K(T)$ function by an Arrhenius expression; by then rearranging and taking the integral and logarithm of the resulting expression it is possible to plot $\ln t$ vs T^{-1} at a given conversion so that the slope gives the value of activation energy. Thus, values of activation energy at several conversions can easily be calculated. Fig. 4 shows the $\ln t - T^{-1}$ plot for the chlorination of Fe_2O_3 for a conversion of 0.3, between 600 and 950°C, keeping other experimental conditions constant. In the left inset plot $\ln t$ vs T^{-1} curves are also shown for various conversions. Curves are partially parallel, which means that there is no change in the reaction mechanism when the reaction proceeds. Therefore, in order to improve clarity in the discussion we will only analyze in this figure and in the following the effect of temperature on curves corresponding to $\alpha = 0.3$, assuming that the conclusions are valid for all conversions. Thus, Fig. 4 shows such a curve. A good linear correlation between 600 and about 750°C is observed as indicated in the plot by a straight line. The good linear fit between 600 and about 750°C indicates that the kinetic regime is the same for the whole temperature range. The activation energy in this region is 200 kJ mol^{-1}. In a first analysis this high value is credible if the rate-controlling step is that of the chemical reaction or by a combination of pore diffusion and chemical reaction. In order to distinguish between both possibilities it is

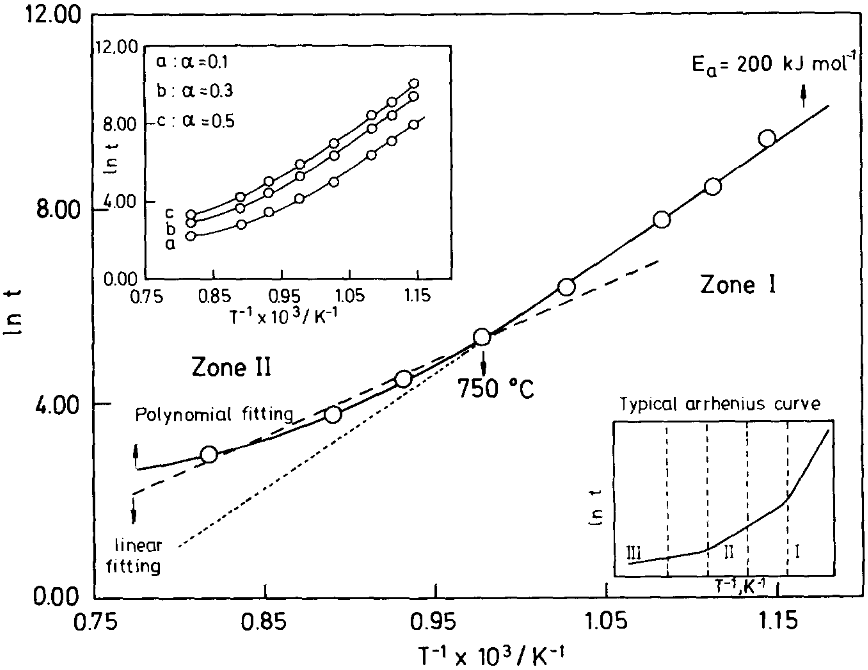

Fig. 4. Plot of $\ln t$ vs T^{-1} for conversion of 0.3 (flat crucible). Left inset plot represents curves at various conversions. Right inset plot shows typical Arrhenius behavior for solid gas reactions involving powders.

necessary to analyze the rest of experimental results. It is observed that when the temperature increases above 750°C experimental points progressively deviate from the extrapolation of the straight line, as indicated by the line of points in Fig. 4. The deviation from linearity increases with the temperature. Certainly, as usually interpreted, a different kinetic behavior with the temperature must be understood as a change in the controlling regime. Therefore, a change in the nature of the slowest reaction step takes place above 750°C. Runs above 750°C can be fitted by using two approaches, which have different physical meaning. One way is by means of the best line, and the another by a polynomial. When points above 750°C are fitted by the best straight line, as shown by the lines of points in Fig. 4, an activation energy of 125 kJ mol^{-1} is obtained. In order to interpret this fitting it is convenient to see the typical Arrhenius curve expected for solid-gas reactions involving reacting powders, which is shown in the right inset plot of Fig. 4. Three different controlling regimes depending on the temperature are possible when no change is expected in the reaction path. The three reaction zones are described as zone (I), chemical control, zone (II), mixed control (pore diffusion and chemical reaction) and zone (III) gas-diffusion control. The apparent activation energy for zone (II) is generally about one-half of the intrinsic activation energy determined in zone (I) [3]. A comparison between the inset plot and the experimental curve indicates that the typical behavior is not observed in this study. In fact, the value of E_a for temperatures above 750°C, viz. 125 kJ mol^{-1}, is not one-half the value of 200 kJ mol^{-1}, as would be expected for a change from chemical to mixed control as the temperature rises. Since no evidence of a change in the reaction path with temperature has been reported, we also disregard a change in the reaction path above 750°C. Finally, the bad fit of the straight line above 750°C indicates that a polynomial fitting might be a better approach. Thus, points above 750°C were fitted by a polynomial, as shown by the full line in Fig. 4. The physical meaning can be understood by reference to the results presented in Figs. 1 and 3. We saw in Fig. 1 and through the data given in Table 1 that runs above 750°C are affected by convective mass transfer, which was also supported by the low dependence of chlorination rate on temperature above 750°C, as shown in Fig. 3. Therefore, as the temperature increases above 750°C the reaction is more affected by convective mass transport and thus points deviate further from linearity, giving a polynomial fit.

Consequently, the plot shown in Fig. 4 can be divided into two zones. Zone I taking place below 750°C and Zone II, above that temperature. The high value of E_a determined in Zone I may suggest chemical control. But taking into account that diffusion into the sample pores could be even important (see Fig. 2B), mixed control (chemical and diffusion into the sample pores) is also possible. On the other hand, zone II should be affected by convective mass transfer into the film surrounding the sample. In order to verify these hypotheses more experiments were performed, as shown in Fig. 5, which shows ln t–T^{-1} curves for several experimental conditions. Curves 1, 2, and 3 correspond to chlorinations of several thicknesses of samples at a constant flow rate of 4.55 L h^{-1} and a $pCl_2 = 35$ kPa (empty circles). Experiments plotted in curve 1 correspond to chlorinations of 2 mg of sample contained within the flat crucible. Curve 2 represents experiments performed with 10 mg also contained within the flat crucible and curve 3 corresponds to chlorinations of 40 mg of sample contained within

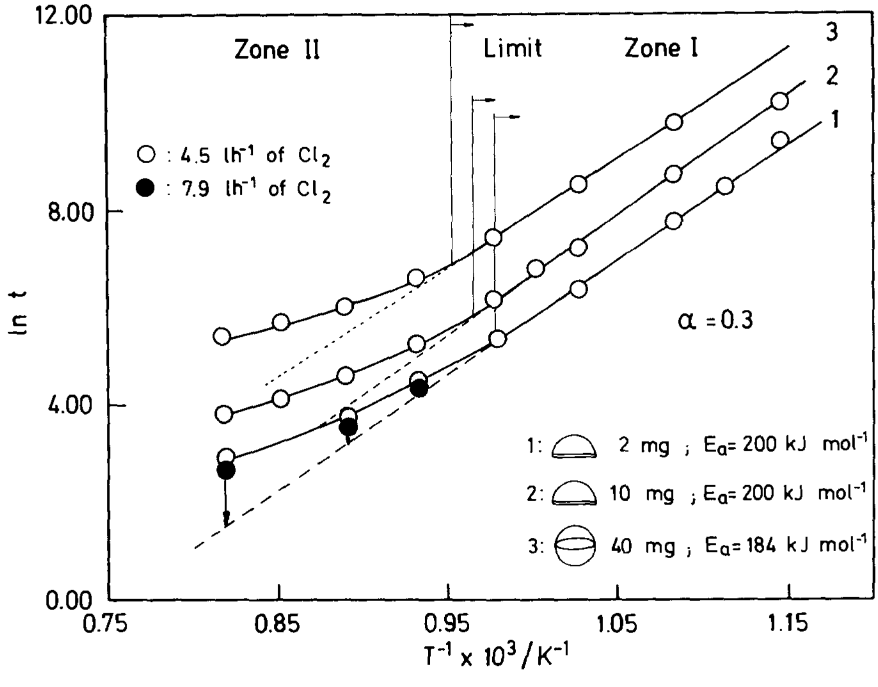

Fig. 5. Plot of ln t vs T^{-1}. Curve 1: 2 mg of Fe_2O_3 (flat crucible; curve 2: 10 mg of Fe_2O_3 (flat crucible); Curve 3: 40 mg of Fe_2O_3 (hemispherical crucible). Black circles refer to runs performed with a flow rate of 7.9 L h^{-1} and other experimental conditions the same as those used for curve 1.

the hemispherical crucible, in which the rate of mass transfer into the sample pores is substantially decreased. Black circles are values of ln t vs T^{-1} for chlorinations performed with a greater flow rate of 7.9 L h^{-1} but with other experimental conditions the same as those used for the empty circles of curve 1.

A comparison of the zone I for the three curves shows that the linear behavior is approximately the same, i.e. the slope is very similar. The corresponding activation energies for lines 1, 2, and 3 are 200, 200 and 184 kJ mol^{-1}, respectively. To a first approximation, this indicates that the rate-controlling regime is not significantly changed as the sample mass increases. However, higher values of ln t at the same temperature as the sample thickness increases, curves 1 to 3 (Fig. 5), indicate that r decreases as the sample mass increases. Consequently, the rate-controlling regime is depending on mass transport into the sample pores over all the temperature range studied. This feature, together with the fact that the high value of E_a is practically constant, certainly indicates that the reaction is under mixed control for the three curves in Zone I.

As the sample mass increases the extent of linear zone, i.e. Zone I, is shifted to higher temperatures. This is in agreement with the fundamental reason leading to a change in the rate-controlling regime as the temperature increases: convective mass transfer. As the sample mass increases the overall reaction rate is slower and thus the effect of convective mass transfer becomes relevant at higher temperatures. Black circles shown in Fig. 5 confirms that above 750°C the reaction rate is significantly affected by convective mass transfer since they correspond to experiments performed with a higher flow rate. We notice that black points are shifted to lower values of ln t, showing a tendency to fit the extrapolation of straight line obtained at low temperatures. As the temperature inceases the effect of the flow rate is more important.

According to these results, it is concluded that the reaction changes from mixed control at low temperatures, Zone I, to mixed control strongly affected by convective mass transfer above 750°C, Zone II. The reaction is not under pure diffusion control in the gaseous phase even at the higher temperature studied, i.e. 950°C. Also pure chemical control for 2 mg of sample is not observed at temperatures as low as 600°C, at which the reaction becomes very slow.

4.3. *Study of the effect of the presence of inert material: TiO_2 and Al_2O_3 powders*

In theory, by using a very small amount of Fe_2O_3 powder the thickness of the sample would be decreased so that the rate-controlling regime should change from mixed to chemical control. A sample mass lower than 1 mg might be advisable. However, it is known that the use of small samples must be undertaken judiciously since sample masses below 1 mg may lead to low reproducibility and increasing experimental error in the determination of the reaction rate. Moreover, packing of the powder of Fe_2O_3 may be the fundamental reason of the mixed control observed in the reaction. For this reason, experiments were carried out using very small samples of Fe_2O_3 mixed with chemically inert powders. Thus, a small amount of Fe_2O_3 contained in 2 mg of a mixture can be studied without the inconvenience of handling small samples since the mixture can be well accommodated within the crucible enabling good dispersion and thus a good free-diffusion accessibility of the reacting gas. Moreover, a mixture of inert and reacting powders facilitates the disintegration of the agglomerates of the latter and thus the tightness of packing is decreased, enhancing the reacting gas diffusion.

Titanium and aluminium oxides have high thermodynamic stability. They are difficult to chlorinate at low temperatures since the corresponding values of ΔG°, as a function of the temperature, are given by: $\Delta G^\circ_{TiO_2} = -0.02836\,T + 85.345$ and $\Delta G^\circ_{Al_2O_3} = -0.06744\,T + 165.455\,\mathrm{kJ\,mol^{-1}}$, respectively [14]. Therefore these oxides were chosen as inert powders. Mixtures of 2 mg of Fe_2O_3–TiO_2 and Fe_2O_3–Al_2O_3 were prepared with the weight ratios 3/7 and 1/4, respectively. Fig. 6 shows the corresponding chlorination curves for both mixtures at several temperatures. In the same figure the chlorination of 2 mg of pure Fe_2O_3 is plotted. It is noted that there are noteworthy differences between the reaction times for each experiment. The chlorination of 2 mg of pure Fe_2O_3 is slower than those corresponding to 0.6 and 0.4 mg of Fe_2O_3 mixed with TiO_2 and Al_2O_3 powders, respectively. In addition, the chlorination of 0.6 mg is also slower than that for 0.4 mg. In order to verify that the rate-controlling regime was mixed even for the 0.4-mg sample, ln t vs T^{-1} was plotted, as shown in Fig. 7. For comparison, the curve corresponding to the chlorination of 2 mg of Fe_2O_3 is shown in the same figure. The comparison is performed in Zone I, between 600–750°C. It is noted that activation energy is not modified within ± 15%, which is reasonable for

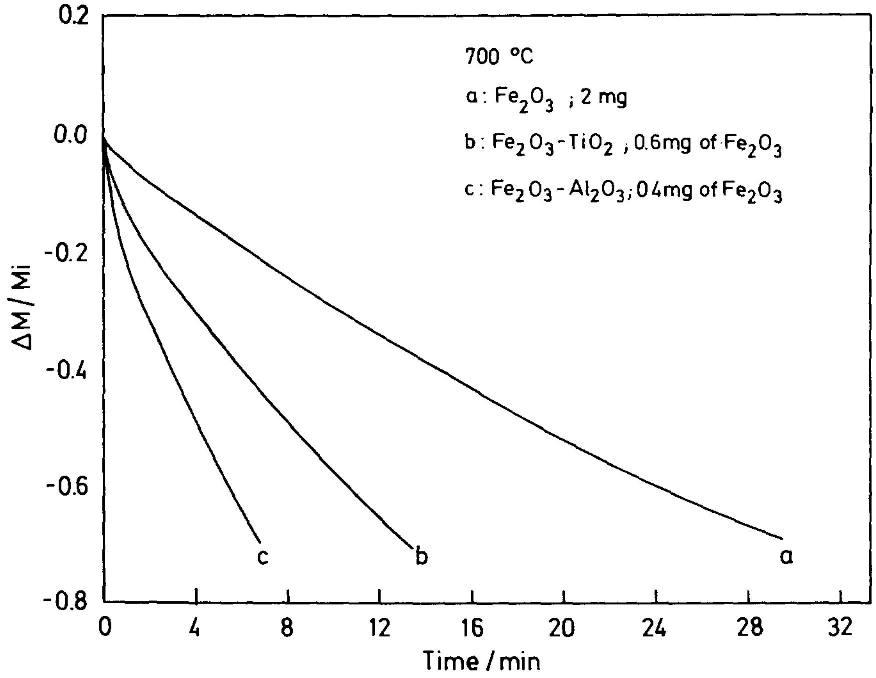

Fig. 6. Effect of chemically inert powders on the chlorination of Fe_2O_3 at 700°C (flat crucible).

calculations of activation energies. According to this result we conclude that reducing the thickness of the sample and the tightness of packing by using inert powders produces no changes in the controlling regime. Therefore, the reaction is under mixed control even for very small samples.

We concluded from this study that even under extreme conditions of low temperature and very small sample mass, the chlorination of Fe_2O_3 is under mixed control. An elementary chemical step and the diffusion of gases into the sample pores are rate-limiting. It is interesting to note that the rate-controlling mass transport is not eliminated even at low temperatures, where the intrinsic reactivity of the solid is very low. This may be a consequence of the chlorination of Fe_2O_3 at low temperature being reversible, as indicated above by the corresponding value of ΔG°. Thus, the reversal of reaction (I), i.e, the reaction of $O_2(g)$ with $Fe_2Cl_6(g)$ or with $FeCl_3(g)$, produces new Fe_2O_3 within the sample pores. The reverse reaction is favored as the residential time of the gaseous products increases, which in turn is a consequence of the packing of the particles of Fe_2O_3 and thickness of the sample. Consequently, diffusion out of gaseous products may be considered as the slowest diffusion step controlling overall chlorination. On the other hand, it is not possible to propose the nature of the slowest chemical step, since the reaction path is unknown. However, it may be assumed that the E_a under chemical control should be near to 400 kJ mol^{-1}, twice the value determined for mixed control, in agreement with the typical kinetic behavior observed by solid–gas reactions, as shown in the right inset plot of Fig. 4.

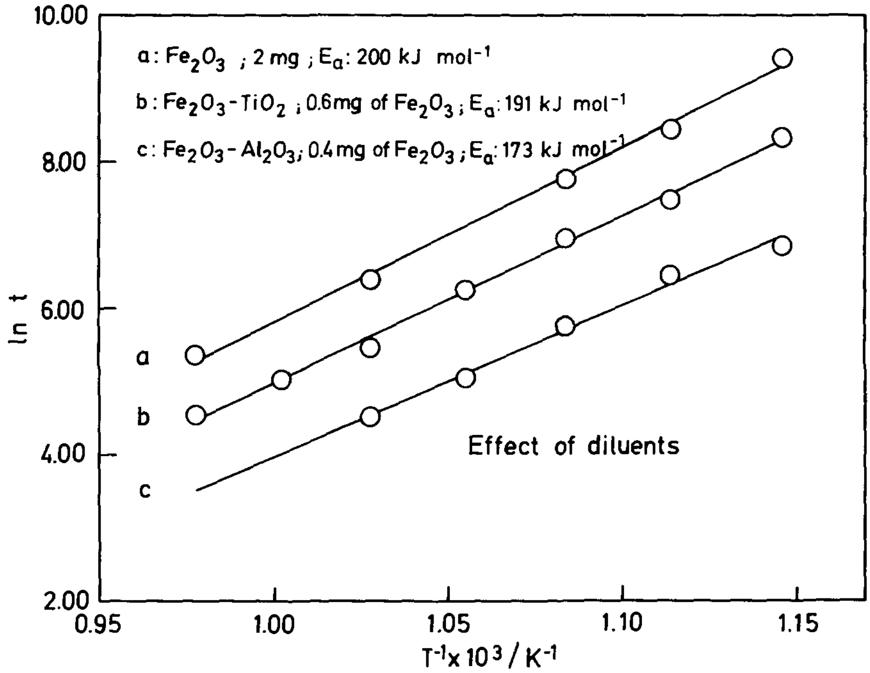

Fig. 7. Plot of ln t vs T^{-1} for the chlorination of 2 mg of (a) pure Fe_2O_3; (b) Fe_2O_3–TiO_2; and (c) Fe_2O_3–Al_2O_3 (flat crucible).

5. Conclusions

Findings presented in this research improve the understanding of the kinetics of the chlorination of Fe_2O_3. It was demonstrated that the reaction is under mixed control even in extreme conditions of low temperature and small sample mass. It is concluded that the influence of mass transport on the reaction rate appears as a characteristic of the reaction system. It may be a consequence of the fact that is very difficult to reach chemical control when the reacting gas flows on a fixed bed of hematite.

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